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(54) Title: EXTRUDED PRODUCTS FROM POLYETHYLENE TEREPHTHALATE WITH REDUCED ACETALDEHYDE CONTENT AND PROCESS OF THEIR PRODUCTION

(57) Abstract: Polyols with at least one primary hydroxy function and at least one other primary, secondary or tertiary hydroxy function in the 2 and/or 3 position are used as additives in concentrations from 50 ppm to 5,000 ppm in order to reduce the acetaldehyde content of extruded products of polyetheylene terephthalate. Sugar alcohols, such as sorbitol, mannitol or xylitol, are preferably used. Additionally, ionic compounds, preferably easily soluble ionic compounds, such as alkali compounds, can be admixed in amounts from 0.05 ppm to 50 ppm. According to the present invention, aqueous polyol solutions are sprayed onto polyethylene terephthalate pellets after polycondensation or after the second polycondensation stage, also known as solid state polymerization, or said pellets are produced through extrusion with a polyol content of less than or equal to 25 percent by weight, pelletized, and admixed as a masterbatch with a polyester prior to processing.

EXTRUDED PRODUCTS FROM POLYETHYLENE TEREPHTHALATE WITH REDUCED ACETALDEHYDE CONTENT AND PROCESS OF THEIR PRODUCTION

The invention relates to extruded products of polyethylene terephthalate with a reduced acetaldehyde content, such as bottles or films, and to a process to produce the same.

Polyethylene terephthalate is largely used as a raw material to produce packaging materials, such as bottles. Specifically the use of polyethylene terephthalate in producing bottles for mineral water requires a very high degree of purity of this polyester. As thermal decomposition of the polyethylene terephthalate occurs when this compound is processed into extruded products, breakdown products will be found in the processed polyester in any case. The free acetaldehyde content is of particular importance for the use as a receptacle for mineral water as even ultramicro-traces of this substance would affect the taste of the mineral water. Acetaldehyde forms during the hydrolysis or alcoholysis of vinyl esters of the terephthalic acid that have formed in a purely thermal process, and is also a product of oxidative polyester degradation.

Basically, there are three preferred resolutions to this problem. A first option is to stabilize the polyester for high processing temperatures. It is known that phosphor compounds are used as stabilizers (JP 58 047 024, JP 53 026 893, JP 62 199 648, WO 97 44 376, EP 826 713, JP 101 82 805, U.S. Patent 5,874,517), and heterocycles have been described as well (JP 57 049 620).

A second option includes the largely complete decomposition of the vinyl esters in the second polycondensation stage, also known as the solid state polymerization (SSP). This is achieved through treatment with water or aliphatic alcohols. Examples of such procedures are found in JP 07 053 698; JP 04 211 424; CH 655 938; U.S. Patent 4 591 629; BE 896 505 and JP 56 055 426.

A third option is to "catch" the free acetaldehyde with appropriate chemical compounds. Among others, polyamides based on xylylene diamine (JP 62 181 336, JP 62 050 328, U.S. Patent 5 258 233), commercial polyamides, such as nylon (EP 714 832, CH 684 537, WO 97 01 427), or special polyamides of terephthalic acid, bis(hydroxymethyl)cyclohexane and bis(aminomethyl)cyclohexane (WO 97 28 218) have been used as "catchers". Inorganic materials, such as zeolites, are also used (U.S. Patent 4 391 971, WO 94 29 378).

The use of polyamides has proven to be the most efficient option. However, these substances have a disadvantage in as far as they cause an undesirable yellow coloring in the polyester.

The known acetaldehyde catchers are added just before the polyester is being proc ssed, that is, immediately before preforms are being produced.

This causes feeding problems.

It is the object of the present invention to clearly reduce the free acetaldehyde content in products of extruded polyethylene terephthalate, which results from the processing process, by adding "catchers" approved for use with foodstuffs, without affecting other parameters of the extruded product, such as the color or mechanical properties, to an unacceptable extent.

Furthermore, it is critical that this addition does not have any negative influence on the conditions under which the modified polyester is being processed and that the modified polymer can be processed as known and without any additional processing steps.

Surprisingly, it was found that the acetaldehyde content of the products can be clearly reduced by adding polyols to polyethylene terephthalate prior to, or during extrusion without affecting the processing criteria or product properties.

It was further established that specifically polyols with at least one primary hydroxy function and one more primary, secondary or tertiary hydroxy function in the 2 and/or 3 position qualify as acetaldehyde catchers for the specified processing parameters.

Relatively low-melting sugar alcohols, such as sorbitol, mannitol or xylitol, are especially suited.

Furthermore, it was found that the free acetaldehyde content in the polyester after processing can be clearly reduced by spraying an aqueous polyol solution onto crystalline polyethylene terephthalate pellets after the second polycondensation stage, which is also known as solid state polymerization. Without this application of an aqueous polyol solution, a drastic reduction of the molecular weight of the polyester through hydrolysis during processing occurs. The modified polyesters can subsequently be processed according to known processes. Spray-application of aqueous polyol solutions immediately following the solid state polymerization provides a simple method for modifying the polyester so that the free acetaldehyde, which is generated through processing, is reduced.

The added polyol amount is between 50 ppm and 2,000 ppm, preferably between 200 ppm and 1,000 ppm. The concentration of the spray solutions is between 5 percent by weight and 70 percent by weight, preferably between 10 percent by weight and 50 percent by weight.

The aqueous polyol solution is sprayed onto the pellets at temperatures between 0°C and 300°C, preferably between 20°C and 220°C.

In addition, polyethylene terephthalate with a polyol content of up to 25 percent by weight can be made through extrusion, and pelletized. Surprisingly, the degradation of the polyester through alcoholysis under the given process conditions in the presence of multivalent alcohols can be reduced to an extent whereby a modified polyester of a viscosity adequate for pelletization is obtained, through a selection of appropriate process conditions, such as retention time and temperature.

Preferred use is made of sugar alcohols, such as sorbitol, mannitol or xylitol.

According to the present invention, the retention time is 20 seconds to 450 seconds, preferably between 30 seconds and 150 seconds, with temperatures ranging from 225°C to 300°C, preferably from 230°C to 285°C.

In the processing stage, the polyester, which has been modified through extrusion, can be added to the polyester resin as masterbatch in order to reduce the free acetaldehyde content.

Furthermore, it was found that adding 0.05 ppm to 50 ppm of ionic compounds (relative to the polyester) increases the efficiency of the polyols as aldehyde catchers while at the same time reducing the slight discoloring of the extruded products that were treated with polyols.

Preferred ionic compounds are readily soluble ionic compounds, more specifically alkali compounds.

With as little as 0.1 ppm to 5.0 ppm of these ionic compounds, the acetaldehyde content of extruded products can be reduced by another approximately 5 to 25 percent.

An especially favorable processing method is to spray aqueous polyol solutions containing the ionic compounds as additional additives onto crystalline polyethylene terephthalate pellets after the second polycondensation stage.

The invention is explained with embodiments below.

The acetaldehyde generation during the processing of polyethylene terephthalate was measured according to the following method:

The polyester was processed on an ES 200-50 injection molding machine by Engel Company, with a screw 30 mm in diameter/and a length-diameter ratio of 20.

The components, that is dried polyethyl n ter phthalate and th polyols, were mixed in a stainless steel vessel through intense stirring, and then fed to the material hopper of the injection molding machine, to which a nitrogen curtain was applied. This mixture was processed (melted and homogenized) at temperatures between 270°C and 300°C. This melt was then injected into a cooled mold under pressure processing parameters:

<u>Drying</u>

Instrument: circulated-air drying oven UT20 by Heraeus Instruments
Temperature: 120°C
Duration: 12 hours

<u>Injection molding</u>

Machine: ES 200-50, by Engel Company
Cylinder temperatures: 277/277/277/277°C
Screw speed: 42 rpm
Cooling time: 10 seconds
Dwell pressure time: 10 seconds
Melt retention time: 2.5 minutes

The acetaldehyde content of the resins produced as described above was determined according to the following method: At first, the various materials were ground with a 1 mm screen in a centrifugal mill by Retsch Company (ZM 1) in the presence of liquid nitrogen. Approximately 0.1 g to 0.3 g of the ground material was put in a 22 mL sample bottle, and sealed with a polytetrafluoroethylene seal. The sample bottles were heated in a temperature-controlled, headspace oven (HS-40 XL headspace autosampler by Perkin Elmer) at 150°C for 90 minutes, and subsequently analyzed through gas chromatography (XL GC AutoSystem by Perkin Elmer) with an external standard.

The calibration curve was prepared through complete evaporation of aqueous solutions of different acetaldehyde contents.

The equipment specifications for the acetaldehyde determination are as follows:

Headspace Autosampler Conditions:

Oven temperature	150°C
Needle temperature	160°C
Transfer temperature	170°C
Retention time	90 minutes

Gas Chromatographical Conditions:

Column	1.8 m by 1/8" stainless steel
Packing	Porapack Q, 80/100 mesh
Carrier gas	nitrogen, 30 mL/minute
Fuel gas	hydrogen
Air	synthetic air
Column temperature	140°C
Detector temperature	220°C

The effect of adding solid polyol to the polyethylene terephthalate prior to processing into extruded products will be explained in the following examples.

Tables I and II show the significant reduction of the acetaldehyde content of the modified polyethylene terephthalate as compared to polyesters to which no polyol was added or to which commercial stabilizers were added respectively. It is interesting to note that polyvinyl alcohol with exclusively secondary alcohol functions can generate acetaldehyde through alcoholysis of the vinyl esters, but that it cannot bond the liberated aldehyde.

Table I

Acetaldehyde Content of Extruded Products of Polyethylene Terephthalate as a Function of Added Solid Additives

Test No.	Added Polyol	Added Amount in ppm	Acetaldehyde Content of the Processed Products in ppm
0 (reference)	-	-	12.7
1	xylitol	2,000	7.1
2	mannitol	2,000	7.3
3	sorbitol	2,000	5.6
4 (reference)	polyvinyl alcohol 3-98	2,000	22.5
5 (reference)	polyvinyl alcohol 15,000	2,000	18.9
6 (reference)	Irganox 1010 (Ciba-Geigy)	2,500	10.1

Table II provides an overview of the dependence of the acetaldehyde content on the concentration of added solid polyols.

Table II
Acetaldehyde Content of Extruded Products of Polyethylene Terephthalate as a Function of the Concentration of Added Solid Additives

Test no.	Added polyol	Add d amount in ppm	Acetaldehyde content of processed products in ppm
0 (reference)	-	-	13.9
1	sorbitol	3,000	4.8
2	sorbitol	2,000	5.8
3	sorbitol	1,000	5.1
4	sorbitol	500	8.1
5	sorbitol	300	7.1
6	mannitol	2,000	7.3
7	mannitol	1,000	6.2
8	mannitol	500	8.2

The behavior as a "comonomer" during processing is of critical importance for the use of appropriate polyols. For this reason, the molecular weight distribution of the processed resins was determined.

To characterize the polyethylene terephthalate samples, 200 mg of the ground resin were dissolved in 5 mL of 1,1,1,3,3,3-hexafluoroisopropanol. Once the polyester had completely dissolved, 100 μL of this solution were adjusted with chloroform in a 2 mL graduated glass flask. These solutions were filtrated and analyzed under the following conditions:

Instruments:

Size exclusion chromatography unit with Polymer Laboratories (PL) HPLC pump LC 1120

Injector Spark Holland Basic Marathon

Degasser Degasys DG 1210

UV/VIS detector PL LC 1200

Column Oven K5 (Tech Lab)

Conditions:

Separating column: 2 columns with PL Gel Mixed B, 10 µm, (300 by 7.5 mm)

Eluting solvent: chloroform

Temperature: 35°C

Detection: 263 nm

Analysis time: 25 minutes

Injected volume: 50 µL

Software:

PL- caliber software

Calibration:

External calibration with polystyrene standards (PL)

Table III below shows the values for the extruded products of polyethylene terephthalate determined through molecular weight determination.

Table III

Molecular Weight Determination for Modified Polyethylene Terephthalate Resins

Additive	Concentration (ppm)	Mw	Mn	IV, calculated (dl/g)
- (reference)	-	60,000	25,900	0.6844
sorbitol	500	58,750	24,850	0.6733
sorbitol	1,000	56,000	23,900	0.6488
sorbitol	3,000	49,100	21,100	0.5860
pentaerythritol	1,000	55,000	24,000	0.6398

It becomes obvious from Table III that there is only a slight decrease in polyester viscosity during processing due to the chain degradation caused by alcoholysis for a polyol addition up to approximately 1,000 ppm. There is no limitation to processing the modified products. No gel formation, that is, the formation of a branched polyester, was observed even when adding by far more than 3,000 ppm of polyol in any case.

Some examples depicting processes according to the invention to produce products of polyethylene terephthalate with a reduced acetaldehyde content through spray-application of aqueous polyol solutions are described below.

The following examples are for illustrative purposes only and are not intended to limit the scope of this invention. Unless otherwise indicated, all parts and percentages are by weight.

Example 1 (reference)

1 kg polyethylene terephthalate pellets with an intrinsic viscosity (IV) of 0.76 dl/g were processed according to the above method on the Engel machine. The resulting polyester resin had a free acetaldehyde (AA) content of 10.5 ppm.

Example 2 (according to the invention)

3 mL of a 10 percent aqueous sorbitol solution were sprayed onto 1 kg polyethylene terephthalate pellets with a intrinsic viscosity of 0.76 dL/g by means of a hand atomizer for thin-layer chromatography (TLC) at a temperature of 25°C.

The polyester resin obtained from subsequent processing on the Engel machine had a free acetaldehyde content of 6.5 ppm (approximately 62 percent of the acetaldehyde contained in the reference).

Example 3 (according to the invention)

Similar to embodiment 2), 5 mL of a 10 percent aqueous sorbitol solution were sprayed onto 1 kg of polyethylene terephthalate pellets with a intrinsic viscosity of 0.76 dL/g at a temperature of 25°C.

After the polyester had been processed on the Engel machine, a free acetaldehyde content of 5.7 ppm was detected (approximately 54 percent of the content of the reference).

Table IV below shows the acetaldehyde content of the polyester resins as a function of the amount and conc ntration of th aqueous sugar alcohol solution. The molecular weight of the poly thylene t rephthalate after processing is shown in addition.

Table IV

Acetaldehyde Content in th Polyethylene Terephthalat after Proc ssing Through Extrusion as a Function of the Amount of the Added Additive and of the Concentration of the Aqueous Additive Solution

Test no.	Sorbitol addition in ppm	Concentration of aqueous solution (percent by weight)	Acetaldehyde (AA) (ppm)	% AA relative to the reference	Mw *	Mn **
1	0	-	10.5	100	59,570	25,460
2	300	10	6.5	61.9	58,330	24,720
3	400	10	5.9	56.2	58,850	24,875
4	500	10	5.7	54.3	58,750	24,650
5	750	10	5	47.6	57,000	24,100
6	1000	10	5.2	49.5	54,900	23,400
7	50	5	9.5	90.5	58,650	25,450
8	100	5	10.5	100	58,600	25,250
9	150	5	8.4	80	58,250	25,100
10	200	5	7.2	68.6	58,000	24,850
11	250	5	6.7	63.8	58,600	24,950
12	500	5	5.3	50.5	57,800	24,250
13	500	25	5.2	49.5	58,100	24,300
14	500	50	5.7	54.3	57,750	24,400

* weight-average molar mass measured with size exclusion chromatography

** number-average molar mass measured with size exclusion chromatography

Table IV illustrates that the acetaldehyde content of polyester resins after processing can be significantly reduced by spraying aqueous polyol solutions on them, specifically sugar alcohol solutions, without considerably reducing their molecular weight, which would affect the properties of the extruded product.

Another option to produce products of polyethylene terephthalate with a low acetaldehyde content is through adding a polyol-containing masterbatch to the processed polyester.

The following tests were conducted to produce polyol-containing polyethylene terephthalate.

1. Compounding by means of ZSK 30

The polyethylene terephthalate used to produce the sorbitol batch was dried at a temperature of 120°C for 20 hours in a SOMOS drying plant TF 100 (by Mann und Hummel ProTec GmbH) with dry air in a closed circuit.

The sorbitol batch was produced on the ZSK 30, a two-shaft laboratory kneading extruder with co-rotating anticlockwise screws, made by Werner und Pfleiderer Company. The screw diameter is 30.7 mm and the screw length is 1,241 mm, which equals 40.4 D. The plasticizing, mixing and dispersing process occurs via 3 kneading element blocks in the compression and metering zones. The metering zone is provided with a vacuum degassing opening. The product was discharged via orifice nozzles.

The d-sorbitol was fed together with the polyethylene terephthalate pellets via feeder 1 to which a permanent nitrogen curtain is applied, or into the compression zone via sidefeeder 2. Precise metering of the individual components was achieved through the use of electronic differential metering balances.

Adding more than 20 percent of sorbitol via the sidefeeder was not feasible as the polyethylene terephthalate melt could not absorb the (liquid) sorbitol which had molten at the hot funnel wall to a large extent.

The processing parameters are shown in Table V below.

Table V
Processing parameters – sorbitol batch
Machine: ZSK 30

	Unit	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4	Sample No. 5
Polyethylene terephthalate C98 d-sorbitol addition	% b.w. % b.w.	100 -	92.5 7.5 sidefeeder 2	90.0 10.0 sidefeeder 2	85.0 15 sidefeeder 2	90.0 10.0 feeder 1
Screw speed Throughput Sorbitol retention time	r.p.m. kg/hr. sec.	200 10 -	200 10 40	200 10 40	200 10 40	200 10 80
Cylinder temp. Actual value T1 - T6 Mass temp.T4/ T6 Pressure (nozzle) Torque Vacuum I.V. Weight-average molecular weight Number-average molecular weight	°C °C bar % dl/g g/mole g/mole	232, 260, 275 285, 284, 282 292, 287 3 79 to 82 -0.9 0.691 68,800 26,080	226, 248, 265 272, 271, 272 279, 278 3 74 to 76 -0.9 - - -	225, 248, 264 273, 272, 272 277, 278 2 70 to 74 -0.9 0.460 37,550 17,350	224, 248, 263 272, 271, 272 275, 278 2 70 to 76 -0.9 0.451 38,350 17,750	220, 246, 264 274, 272, 272 278, 278 2 38 to 43 -0.9 0.459 35,700 16,500

2. Compounding by Means of DSK 42/6

Polyethylene Terephthalate Drying:

The polyethylene terephthalate was dried in a circulated-air drying oven by Binder Company, to which a nitrogen curtain was applied.

Drying temperature: 160°C

Drying time: 6 hours

The sorbitol batch was made on the DSK 42/6 by Brabender Company, an internal counter-rotating twin-screw compounder.

The screw diameter was 43 mm, and the process length 6D. Forced conveying and a narrow r tention time range ar provided by the s nse of rotation of the machine.

D-sorbitol was added together with the polyethylene terephthalate via the nitrogen-purged screw metering unit with speed control.

For concentrations above 3 percent of sorbitol, no uniform feed to the twin-screw compounder via the metering screws was achieved due to polyethylene terephthalate/ sorbitol bonding.

Adjusted processing parameters:
Cylinder temperatures: 265°C/270°C/275°C
DSK screw speed: 80 rpm
Screw metering speed: 5 rpm
Throughput: 3kg/hour

3. <u>Compounding in W50 EHT Measuring and Kneading Chamber</u>

<u>Polyethylene Terephthalate Drying</u>:

The polyethylene terephthalate was dried in a circulated-air drying oven by Binder Company, to which a nitrogen curtain was applied.

Drying temperature: 160°C

Drying time: 6 hours

The addition of sorbitol to the polyethylene terephthalate was simulated by means of the W50 EHT measuring kneader by Brabender Company.

Measuring kneaders are used to test processes, such as mixing, compounding or plasticizing of polymers, chemicals or additives, under production-geared conditions. The dried polyethylene terephthalate was fed to the kneading chamber together with the d-sorbitol, and a nitrogen curtain was applied during kneading.

Concentrations above 40 percent of d-sorbitol could not be added to the polyethylene terephthalate under the following experimental conditions. A separate, molten sorbitol was also found when the kneading chamber was opened to remove the material.

Kneading chamber volume: 55 cm^3
Kneading machine temperature: 240°C
Mass temperature: 247°C
Kneading blade speed: 60 rpm

Table VI shows the results gained from acetaldehyde generation achieved through the addition of a polyethylen terephthalate /sorbitol batch during poly ster processing.

Table VI
Use of Sorbitol-Containing Polyethylene Terephthalate as a Masterbatch to Reduce the Acetaldehyde Generation During polyester Processing.

Test no.	Batch processing	Percent by weight of sorbitol in the masterbatch	Sorbitol concentration in the polyethylene terephthalate (ppm)	Acetaldehyde (ppm)
1	-	0	0	10.9
2	DSK 42/6	0.3	500	5.1
3	DSK 42/6	0.5	500	6.1
4	DSK 42/6	1.5	500	5.3
5	DSK 42/6	3	500	5.6
6	ZSK 30	7.5	500	5.7
7	ZSK 30	10	500	6.5
8	ZSK 30	15	500	6.2
9	ZSK 30	15	1,000	4.9

These tests illustrate that the acetaldehyde content can be significantly reduced by adding polyol-containing polyethylene terephthalate to the polyester to be processed.

Table VII shows the results for the reduction of the acetaldehyde content through spraying polyol solutions, to which additionally ionic compounds were admixed, onto the polyester at room temperature.

Table VII illustrates the effect of ionic compounds in the range from 1 ppm to 50 ppm.

If the polyethylene terephthalate is treated with aqueous polyol solutions at higher temperatures, the polyols will be less efficient in reducing the acetaldehyde content of the extruded products, and the processed polyesters will be slightly colored. Adding ionic compounds will increase the efficiency of the polyols and reduce the slight coloring of the processed polyesters.

Table VIII summarizes these results and illustrates the surprising effect of ionic admixtures with regard to the color of the processed polyesters and the efficiency of the polyols as aldehyde catchers.

The addition of polyols constitutes a simple method of significantly reducing the acetaldehyde content of extruded products made of polyethylene terephthalate resins. Surprisingly, it was found that the addition of ionic compounds in the range from 0.1 ppm to 100 ppm further increas s the ffici ncy of th polyols as aldehyde catchers and that the slight

colorings can b reduced by spraying aqueous solutions of these additives on the polyethylene terephthalate pellets at higher temperatures.

Naturally, the subject process to reduce the acetaldehyde content in extruded products of polyethylene terephthalate can be used alone, or together with other methods to reduce the acetaldehyde content, such as the inclusion of comonomers to reduce the processing temperatures, the use of special catalysts, or the deactivation of catalysts. In addition, combinations of different acetaldehyde catchers, such as polyol/polyamide, can be used to reduce the acetaldehyde content in extruded products made of polyethylene terephthalate.

Table VII

Acetaldehyde Content of Polyester Resins Onto Which Aqueous Polyol/Additive Solutions Were Sprayed at Room Temperature.

Test no.	Polyol	Concentration (ppm)	Additive	Concentration (ppm)	Acetaldehyde (ppm)	Acetaldehyde in % relative to the reference without alkali additive
1 (reference)	-	-	-	-	12.1	
2 (reference)	sorbitol	500	-	-	5.7	100
3	sorbitol	500	sodium hydroxide	100	6.2	109
4	sorbitol	500	sodium hydroxide	50	5.2	91
5	sorbitol	500	sodium hydroxide	10	5.3	93
6	sorbitol	500	sodium hydroxide	5	5.1	89
7	sorbitol	500	sodium carbonate	1	5.3	93
8	sorbitol	500	sodium carbonate	0.5	5.3	93
9	sorbitol	500	sodium chloride	1	4.8	84
10	sorbitol	500	disodium terephthalate	0.5	5.4	95
11	sorbitol	500	sodium benzoate	1	4.9	86

Table VIII

Acetaldehyde Content of Polyester Resins onto Which Aqueous Polyol/Additive Solutions Were Sprayed at 100°C.

Test no.	Polyol	Concentration (ppm)	Additive	Concentration (ppm)	Acetaldehyde content (ppm)	Acetaldehyde content in % relative to the reference without additive (% without sorbitol addition)	Color Δ b*
1 (reference)	-	-	-	-	11.8	- (100)	0
2 (reference)	sorbitol	500	-	-	8.1	100 (69)	+ 1.45
3	sorbitol	500	sodium carbonate	5	4.5	56 (38)	+ 1.14
4	sorbitol	500	sodium carbonate	1	5.2	64 (44)	+ 0.8
5	sorbitol	500	sodium carbonate	0.5	5.3	65 (45)	+ 0.65
6	sorbitol	500	sodium carbonate	0.1	5.9	73 (50)	+ 0.64
7	sorbitol	1,000	sodium carbonate	1	4.8	59 (41)	+ 1.53
8	sorbitol	500	ammonium carbonate	5	6	74 (51)	+ 1.07
9	sorbitol	500	sodium chloride	1	5	62 (42)	+ 0.72
10	sorbitol	500	sodium benzoate	1	5.6	69 (47)	+ 0.8
11	sorbitol	500	disodium terephthalate	0.5	5.2	64 (44)	+ 0.76
12	sorbitol	500	potassium carbonate	5	5.1	63 (43)	+ 1.24

Claims:

1. Extruded products with a reduced acetaldehyde content, characterized as comprising an admixture of a polyethylene terephthalate with a polyol having at least one primary hydroxy function and at least one other primary or secondary or tertiary hydroxy function in the 2 and/or 3 position, in a concentration of from 50 ppm to 5,000 ppm relative to the polyethylene terephthalate are used as additives to reduce the acetaldehyde content, optionally, further admixed with 0.05 ppm to 50 ppm (relative to the polyethylene terephthalate) of at least one ionic compound.

2. Extruded products according to Claim 1, characterized by the fact that the polyol additives are sugar alcohol, such as sorbitol, mannitol or xylitol.

3. Extruded products according to Claims 1 and 2, characterized by the fact that the polyols are preferably used in concentrations from 100 ppm to 2,000 ppm relative to the polyethylene terephthalate.

4. Extruded products according to Claim 1, characterized by the fact that 0.1 ppm to 5.0 ppm of ionic compounds, relative to the polyethylene terephthalate, are admixed.

5. Extruded products according to Claims 1 and 2, characterized by the fact that the at least one ionic compound is an easily soluble compound, preferably an easily soluble sodium compound.

6. A process to produce extruded products of polyethylene terephthalate with a reduced acetaldehyde content, characterized by the fact that aqueous polyol solutions, to which ionic compounds may be admixed, are sprayed onto polyethylene terephthalate pellets.

7. A process to produce extruded products of polyethylene terephthalate according to Claim 6, characterized by the fact that aqueous polyol solutions are sprayed onto crystalline polyethylene terephthalate pellets after post condensation.

8. A process to produce extruded products of polyethylene terephthalate according to Claims 6 and 7, characterized by the fact that aqueous polyol solutions are sprayed onto the pellets of polyethylene terephthalate at temperatures between 0°C and 300°C, preferably between 20°C and 260°C.

9. A process to produce extruded products of polyethylene terephthalate according to Claims 6 through 8, characterized by the fact that the aqueous polyol solution is an aqueous solution of sorbitol, mannitol, xylitol or of combinations thereof.

10. A process to produce extruded products of polyethylene terephthalate according to Claims 6 through 9, characterized by the fact that the amount of polyol added is in the range from 50 ppm to 2,000 ppm, preferably from 200 ppm to 1,000 ppm, relative to the amount of polyethylene terephthalate.

11. A process to produce extruded products of polyethylene terephthalate according to Claims 6 through 10, characterized by the fact that the concentration of the aqueous polyol spray solution is in the range from 5 percent by weight to 70 percent by weight, preferably from 10 percent by weight to 50 percent by weight.

12. A process to produce extruded products of polyethylene terephthalate with a reduced acetaldehyde content, characterized by the fact that polyethylene terephthalate pellets with a polyol content of less than or equal to 25 percent by weight are produced through extrusion, and pelletized and admixed as a master batch with a polyester prior to processing.

13. A process to produce extruded products of polyethylene terephthalate with a reduced acetaldehyde content according to Claim 12, characterized by the fact that retention times of from 20 seconds to 450 seconds, preferably from 30 seconds to 150 seconds, are used to prepare the batch.

14. A process to produce extruded products of polyethylene terephthalate with a reduced acetaldehyde content according to Claims 12 and 13, characterized by the fact that the processing temperatures are in the range from 225°C to 300°C, preferably from 230°C to 285°C.

15. A process to produce extruded products of polyethylene terephthalate with a reduced acetaldehyde content according to Claims 12 through 14, characterized by the fact that sugar alcohols, such as sorbitol, mannitol or xylitol, are used as a polyol.

16. A process to produce extruded products of polyethylene terephthalate with a reduced acetaldehyde content according to Claims 12 through 15, characterized by the fact that polyols are used in the range from 0.5 percent by weight to 50 percent by weight relative to the amount of the polyethylene terephthalate.

INTERNATIONAL SEARCH REPORT

Int tonal Application No
PCT/US 00/17996

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08K5/15 C08J3/205

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08K C08L C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 394 470 A (WERNER MARCEL A ET AL) 19 July 1983 (1983-07-19) column 3, line 16; claims; example 7	1-5
X	EP 0 691 370 A (MITSUBISHI CHEM CORP) 10 January 1996 (1996-01-10) page 2, line 50 -page 4, line 44; claims; tables 1-3	1-5
X	US 4 873 279 A (NELSON LINDA H) 10 October 1989 (1989-10-10) column 8, line 46-52; examples	1-5
X	EP 0 590 647 A (UNION CARBIDE CHEM PLASTIC) 6 April 1994 (1994-04-06) page 5, line 50; examples abstract	6-8

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 October 2000	07/11/2000

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INTERNATIONAL SEARCH REPORT

Int ional Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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